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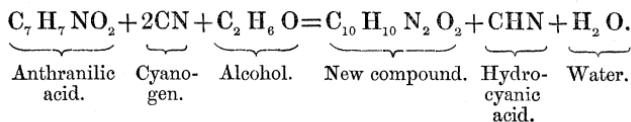
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V. "On the Action of Cyanogen on Anthranilic Acid."  
By P. GRIESS, F.R.S. Received June 29, 1869.

Some time ago\* I pointed out the action which takes place when cyanogen gas is passed into an alcoholic solution of amidobenzoic acid. The principal product of this reaction is, as I have shown, a yellow compound of cyanogen and amidobenzoic acid of the formula  $C_7H_5(NH_2)O_2$ ,  $2CN$ , which separates in large quantities as soon as the alcoholic solution of amidobenzoic acid is nearly saturated with cyanogen. When anthranilic acid, a body isomeric with amidobenzoic acid, is submitted under the same condition to the same reagent, a totally different reaction takes place. In this case the solution remains either perfectly clear, or only traces of a similar yellow compound are precipitated. By allowing the alcoholic solution of anthranilic acid, saturated with cyanogen, to stand for several days, the acid is almost entirely converted into a new compound of the empirical formula  $C_{10}H_{10}N_2O_2$ ; two other new compounds (an acid and an indifferent body) are at the same time formed. It is worthy of remark that none of these compounds are isomeric with any of the bodies which by the same process are formed from amidobenzoic acid. Each of them belongs to a perfectly different type.

I propose on this occasion to treat only of the principal product of the reaction, viz. the compound  $C_{10}H_{10}N_2O_2$ . It is prepared in the following manner. An alcoholic solution of anthranilic acid is saturated with cyanogen gas and left to stand for about eight days. The alcohol is then evaporated at a low temperature, and the crystalline residue washed several times with dilute solution of carbonate of ammonia, by which any traces of the new acid (one of the by-products of the reaction) are removed. It is then further purified by recrystallization from alcohol with the addition of a little animal charcoal. The indifferent body already referred to, which is very little soluble in alcohol, is thus separated. The new compound,  $C_{10}H_{10}N_2O_2$ , is then obtained in the form of white acicular crystals, which are very little soluble in boiling water, but dissolve readily in boiling alcohol and ether. It fuses at  $173^\circ C.$ , and can be distilled in small quantities without undergoing decomposition. Its formation may be expressed as follows:—

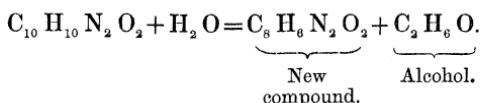


According to this equation, alcohol as well as anthranilic acid and cyanogen take place in the reaction. Confirmatory experiments which I have made show that the compound in question is really an ether.

*Action of Hydrochloric Acid upon the Compound  $C_{10}H_{10}N_2O_2$ .*—Ordinary hydrochloric acid dissolves this body, and when cold does not act upon it. On boiling, however, speedy decomposition sets in and a new

\* Zeitschrift für Chemie. New series, vol. iii. p. 533, and vol. iv. p. 389.

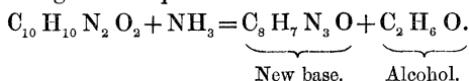
body separates, the formation of which is represented by the following equation :—



This new compound,  $\text{C}_8\text{H}_6\text{N}_2\text{O}_2$ , is very difficultly soluble in boiling water, alcohol, and ether, and crystallizes in small white brilliant plates. It is likewise dissolved by solutions of caustic alkalies, but is again, however, separated by carbonic acid. On adding a solution of silver salt to its aqueous or alcoholic solution (neither of which has any action on vegetable colours), a white precipitate is formed. Fuming nitric acid converts this body into a nitro-compound, crystallizing in honey-yellow prisms of the composition  $\text{C}_8\text{H}_6(\text{NO}_2)\text{N}_2\text{O}_2$ . On treating the latter with sulphide of ammonium or with tin and hydrochloric acid, it is reduced and furnishes a basic amido-compound crystallizing in slightly yellowish-tinted needles, difficultly soluble in all neutral liquids. Its composition is  $\text{C}_8\text{H}_5(\text{NH}_2)\text{N}_2\text{O}_2$ . Compounds of this amido-body with acids crystallize well generally, but are for the most part difficultly soluble.

*Action of Ammonia on the Compound  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2$ .*—On digesting the body for several days at  $100^\circ\text{C}$ . in sealed tubes with alcoholic ammonia, it is gradually converted into a base, almost insoluble in water and difficultly soluble in boiling alcohol ; from this it crystallizes in brilliant nacreous plates.

Its composition agrees with the formula  $\text{C}_8\text{H}_7\text{N}_3\text{O}$ , and its formation takes place according to the equation



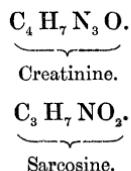
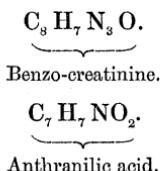
This new base is monacid. Its nitrate is especially characteristic, for it is almost insoluble in water and alcohol. It separates out from very dilute solutions of the base in the form of small white plates on the addition of nitric acid. Its platinum-salt crystallizes in thick yellow needles, and has the composition  $2(\text{C}_8\text{H}_7\text{N}_3\text{O}), 2\text{HCl}, \text{PtCl}_4$ .

The compounds just described may one and all be viewed as substitution products of anthranilic acid, viz. :—

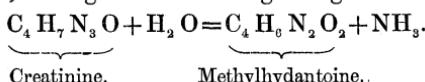
Anthranilic acid .....	$\text{C}_7\text{H}_7\text{NO}_2$	$= \text{C}_7\text{H}_6\text{NO.HO.}$
New ether .....	$\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2$	$= \text{C}_7\text{H}_5(\text{CN})\text{NO.C}_2\text{H}_5\text{O.}$
Product of decomposition of the former with $\text{HCl}$ .....	$\text{C}_8\text{H}_6\text{N}_2\text{O}_2$	$= \text{C}_7\text{H}_5(\text{CN})\text{NO.HO.}$
Nitro-compound .....	$\text{C}_8\text{H}_5(\text{NO}_2)\text{N}_2\text{O}_2$	$= \text{C}_7\text{H}_4(\text{NO}_2)(\text{CN})\text{NO.HO.}$
Amido-compound .....	$\text{C}_8\text{H}_5(\text{NH}_2)\text{N}_2\text{O}_2$	$= \text{C}_7\text{H}_4(\text{NH}_2)(\text{CN})\text{NO.HO.}$
Base obtained from the ether by the action of $\text{NH}_3$ .....	$\text{C}_8\text{H}_7\text{N}_3\text{O}$	$= \text{C}_7\text{H}_5(\text{CN})\text{NO.H}_2\text{N.}$

As I intend taking an early opportunity of considering the rational constitution of these bodies somewhat more fully, I content myself for the

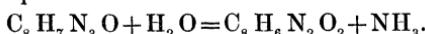
present with remarking that I am inclined to regard the base  $C_8H_7N_3O$  as the creatinine of the benzoic series; it stands to anthranilic acid exactly in the same relation as creatinine "par excellence" does to sarcosine:—



Herr Neubauer has shown\* that creatinine, when treated in a sealed tube with baryta-water, undergoes the following change:—



I consider it highly probable that the base  $C_8H_7N_3O$  will split up in like manner with the formation of the above-described compound  $C_8H_6N_2O_2$ , according to the equation



Indeed this latter compound exhibits great resemblance in its chemical deportment to the methylhydantoin of Herr Neubauer.

In conclusion, I should point out that the azodioxindol described by Herrn Baeyer and Knop in their paper on indigo-blue\* is isomeric with the before-mentioned compound,  $C_8H_6N_2O_2$ . These two bodies show, moreover, great similarity in other respects, so much so that I should feel inclined to view them as identical if their fusing-points did not differ essentially. Herrn Baeyer and Knop state that the fusing-point of their azodioxindol is  $300^{\circ}\text{C}.$ , while the compound I obtained fuses above  $350^{\circ}\text{C}.$  Should it turn out, however, on further investigation that the two bodies are identical, the compound  $C_8H_6N_2O_2$  would have to be regarded as the first derivative of indigo which has ever been prepared synthetically, and which, like indigo-blue itself, contains eight atoms of carbon.

## VI. "On the successive Action of Sodium and Iodide of Ethyl on Acetic Ether." By J. ALFRED WANKLYN, F.C.S. &c. Communicated by Professor WILLIAMSON. Received July 16, 1869.

In a remarkable paper which appeared in the *Philosophical Transactions*, vol. clvi. p. 37 (1866), Frankland and Dupper described the products obtained on treatment with iodide of ethyl of the yellow wax-like mass given by the action of sodium on acetic ether. Besides the description of the compounds, Frankland and Dupper give a theory of their origin,

\* *Ann. der Chem. und Pharm.* vol. cxl. p. 26.